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(71) BASF AKTIENGESELLSCHAFT,  
D-67056, LUDWIGSHAFEN, XX (DE).

(72)

STUVEN, UWE (DE).  
DANIEL, THOMAS (DE).  
FRENZ, VOLKER (DE).  
ENGELHARDT, FRIEDRICH (US).  
FUNK, RUDIGER (DE).

(74)

BORDEN LADNER GERVAIS LLP

(54) POLYMERES GONFLANTS RETICULES

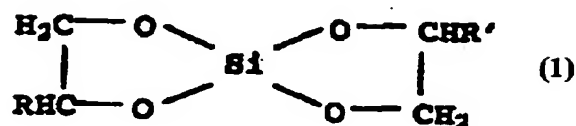
(54) CROSS-LINKED POLYMERS CAPABLE OF SWELLING

(57)

The invention relates to a method for surface cross-linking particles of superabsorbent polymers, characterized by the use of compounds of formula (1) as cross-linking agents, where R and R' independently of each other are hydrogen or C1-C6 alkyl.



(72) FUNK, RUDIGER, DE  
(72) FRENZ, VOLKER, DE  
(72) STUVEN, UWE, DE  
(72) ENGELHARDT, FRIEDRICH, US  
(72) DANIEL, THOMAS, DE  
(71) BASF AKTIENGESELLSCHAFT, DE  
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(54) **POLYMERES GONFLANTS RETICULES**  
(54) **CROSS-LINKED POLYMERS CAPABLE OF SWELLING**



(57) L'invention concerne un procédé pour la réticulation superficielle de particules de polymères superabsorbants, caractérisé par l'utilisation de composés de la formule (1) comme réticulants, formule dans laquelle R et R' représentent, indépendamment l'un de l'autre, hydrogène ou alkyle C<sub>1</sub>-C<sub>6</sub>.

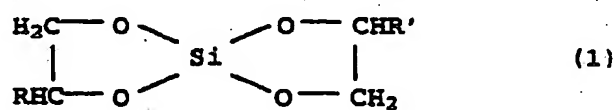
(57) The invention relates to a method for surface cross-linking particles of superabsorbent polymers, characterized by the use of compounds of formula (1) as cross-linking agents, where R and R' independently of each other are hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl.



# Cross-Linked Polymers Capable of Swelling

## Abstract

The invention provides a process for the surface crosslinking of particles of superabsorbent polymers which comprises using compounds of the formula 1 as crosslinkers



in which R and R' independently of one another are hydrogen or C<sub>1</sub>-C<sub>8</sub> alkyl.

## Cross-Linked Polymers Capable of Swelling

The present invention relates to the use of diglycol silicates as crosslinkers in connection with the preparation of carboxyl-comprising hydrogels having improved properties and to the use of the hydrogels thus prepared as  
5 superabsorbents for absorbing aqueous liquids.

Superabsorbents are water-insoluble crosslinked carboxyl-comprising polymers which have the capacity to swell and form hydrogels and so  
10 absorb aqueous liquids and body fluids, such as urine or blood, and to retain the absorbed liquid or fluid volumes under a certain load. They are also referred to as superabsorbent polymers or SAPs.

The preparation and use of such hydrogel-forming polymers is described in  
15 numerous patents, such as EP-A-0 316 792, EP-A-0 400 283, EP-A-0 343 427, EP-A-0 205 674 and DE-A-44 18 818.

In order to prepare polymers which have hydrogels with particularly high liquid absorption capacity, high gel strength and high absorbency under  
20 load it has been found necessary to subject the polymer particles to a subsequent surface treatment. Higher crosslinking close to the surface of the particles of superabsorbent polymers (SAP) is described, for example, in US-A-4 734 478 and US-A-4 666 983. In this context it is preferred to employ substances having two or more groups which are able to form  
25 covalent bonds with the carboxyl groups of the hydrophilic polymers on the particle surface. This is taught, for example, by EP-A-0 349 240.

Crosslinking agents which can be used are polyglycidyl ethers, haloepoxy compounds, polyols, polyamines and polyisocyanates. The surface  
30 postcrosslinking systems known to date can be divided into four groups which act in accordance with different mechanisms:

1. reactive, ring-opening compounds;

2. bifunctional, condensation-active compounds;
3. crosslinking by means of polyvalent metal ions; and
- 5 4. reactive crosslinking by means of a dehydration reaction.

A typical example of crosslinking with a reactive, ring-opening compound is taught by EP-A-0 317 106 through the use of polyglycidyl ethers, such as ethylene glycol diglycidyl ether, and by EP-A-0 618 005, with the use of  
10 polyazetidinium salts. According to DE-A-4 020 780 improved absorbency under load is achieved by surface-crosslinking treatment of a polymer with from 0.1 to 5% by weight of alkylene carbonate.

US-4 666 983 teaches the use of diisocyanates and polyisocyanates as  
15 possible compounds for the postcrosslinking of SAP surfaces. In that case, the reaction with hydroxyl groups produces carbamate structures.

Another option for crosslinking is to form ionic rather than covalent crosslinking points. In accordance with EP-A-0 372 981 polyvalent metal  
20 ions such as aluminum are suitable for the ionic crosslinking of the carboxyl functions.

WO-A-94/09043 describes the use of polyhydroxy compounds, especially organic polyhydroxy compounds, such as diethylene glycol or  
25 trimethylolpropane, with formation of esters at elevated temperature.

EP-A-0 610 013 describes organic esters of carboxyl compounds of a polyfunctional organic alcohol, the description including only partial esterification of the hydroxyl groups. In that case the esters can also be  
30 applied to the SAP surface in a mixture with water or an organic solvent.

EP-A-0 644 207 describes the surface crosslinking of SAP which is porous (through the use of an expansion agent) with polyhydroxy compounds. The crosslinking reaction, however, is entirely analogous to that of

WO-A-94/09043, the sole difference residing in the basic polymer prior to surface postcrosslinking.

5 EP-A-0 509 708 teaches the use of mixtures of a polyhydroxy compound with a surfactant characterized by an HLB of between 3 and 10. In this case the surfactant does not contribute to the reaction but aids the distribution of the polyhydroxy component on the surface.

10 Crosslinking with certain polyfunctional organic alcohols is also disclosed by EP-A-0 450 924.

As has already been set out in EP-A-0 610 013 the processes which operate in accordance with sections 1 - 3 have a number of disadvantages. The crosslinking agents selected from these groups exhibit very high  
15 reactivity and react directly when applied to the polymer that is to be crosslinked. This high reactivity is highly disadvantageous in terms of uniform distribution on the surface. This disadvantage cannot be resolved by increasing the mixing time. Owing to this deficient distribution on the surface, the performance properties fall short of what is ideal.

20 Crosslinking with ionic groups only is very difficult, since in the course of their use diffusion of the polyvalent ions into the SAP particles begins and so severe gel crosslinking rather than surface crosslinking is produced, which has no advantageous performance properties whatsoever.

25 In contrast, the use of organic alcohols or their esters for dehydrating crosslinking in accordance with section 4 does not lead to these disadvantages. Because of the reduced reactivity relative to the polyglycidyl ethers, uniform distribution on the surface of the SAP within a  
30 mixing period is possible. As a result, uniform surface postcrosslinking is able to take place, with the option of controlling the depth of penetration into the SAP particle by way of the mixing time and the dissolving conditions.

The use of alkylene carbonates or polyols of low reactivity, however, has the disadvantage that it is necessary to carry out crosslinking at very high temperatures in order to obtain sufficient reactivity. At such high temperatures there may be thermal postcrosslinking of the entire polymers, which has an adverse effect on centrifuge retention. The high temperatures may also lead to unwanted thermal decomposition of the product, which causes it to discolor.

A process for crosslinking the surface of a superabsorbent polymer by means of a silane coupling reaction with, for example, gamma-glycidyloxypropyltrimethoxysilanes is taught by EP-A-0 195 406. Disclosed are compounds of the formula



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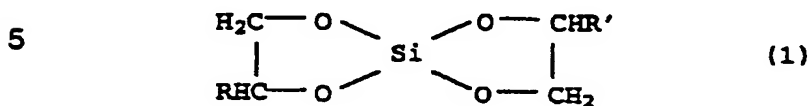
where X is a group which is able to react with carboxyl or carboxylate groups, Y is a hydrolyzable group, and m is 0, 1 or 2.

Primary bonding takes place by means of the reactive group X, with the hydrolyzable group being reacted in the presence of water to form the silanol group which is able in turn, in a further, dehydration step, to form an Si-O-Si bond. However, no compounds are disclosed which consist solely of hydrolyzable groups.

The object of the present invention is to provide a novel process for surface crosslinking by which hydrogels having improved properties in terms of gel strength and water retention capacity are obtained. In this context, the crosslinkers should have a moderate reactivity which allows distribution of the system in question on the surface without the disadvantage of crosslinking only at very high temperatures.

It has surprisingly been found that surface crosslinking with diglycol silicates leads to superabsorbent polymers having the required properties.

The invention therefore provides a process for the surface crosslinking of particles of superabsorbent polymers which comprises using compounds of the formula 1 as crosslinkers



in which R and R' are independent of one another or are the same and are hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl.

10

In formula (1), R and R' preferably have the same meaning and are each, in particular, H or CH<sub>3</sub>.

15 The invention additionally provides water-swellaable hydrogels based on (co)polymerized hydrophilic monomers or on natural hydrophilic polymers, a mixture of these two polymers, or a copolymer in which carboxyl groups are present, which have been surface crosslinked with a compound of the formula 1.

20 The crosslinking reaction generally takes place by means of a transesterification in the relatively high-temperature range. The crosslinking reaction can be accelerated by a catalyst by virtue of which it can be conducted at a lower temperature. Temperatures from 120 to 220°C are preferred for the process of the invention.

25

Crosslinking takes place preferably by transesterification of the compounds of the formula 1, accompanied by ring opening, with the reactive carboxyl groups of the monomers and/or (co)polymers.

30 The compounds of the formula 1 are employed preferably in amounts from 0.05 to 10% by weight, based on the overall monomer weight or on the overall polymer weight. They are preferably used in the form of aqueous, alcoholic or aqueous-alcoholic mixtures.



Suitable natural polymers which can be crosslinked with compounds of the formula 1 to form hydrogels of the invention can be employed either in unrefined or in refined form.

- 5 In particular, carboxymethylpolysaccharides, such as carboxymethylhydroxypropylguar, carboxymethylstarch and alginates, are particularly suitable.

10 Suitable copolymerizable hydrophilic monomers are, in particular, acrylic acid, methacrylic acid, crotonic acid, 2-acrylamido-2-methylpropanesulfonic and -phosphonic acid, vinylphosphonic acid, vinylphosphonic monoesters, salts thereof, acrylamide, N-vinylamides, vinyl acetate, or mixtures thereof. Particular preference is given to using acrylic acid and its salts, e.g. Na, K and/or ammonium acrylate.

15

The polymerization can be carried out by any known reaction, with preference being given to free-radical addition polymerization in a homogeneous phase - for example, in aqueous solution, known as a gel polymerization. Further possibilities for the synthesis of the hydrogels of the invention are offered by precipitation polymerization from organic solvents such as alcohols, preferably tert-butanol or hydrocarbons such as hexane or cyclohexane, or by suspension, dispersion, emulsion or microemulsion polymerization, and also by ionic polymerization.

20

25 The free-radical addition polymerization can be triggered by means of free-radical initiators such as organic or inorganic peroxides and also azo compounds. Examples are benzoyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{O}_2$  and azodiisobutyronitrile. Redox systems are also outstandingly suitable as polymerization initiators.

30

Alternatively, the polymerization can be triggered by high-energy radiation.

The compounds of the formula 1 can be used for crosslinking during the

polymerization reaction and/or not until after the polymerization reaction, for the subsequent crosslinking of the polymer. If the compound of the formula 1 is added only to an uncrosslinked pre(co)polymer, then this is generally done prior to drying by means of homogeneous mixing - for  
5 example, by kneading an aqueous polymer gel in an extruder. Spraying from dilute solution onto a polymer powder or polymer granules is also possible. In this case, targeted crosslinking of the polymers in the vicinity of the particle surface can be conducted by means of an appropriate choice of solvent system.

10

The hydrogels of the invention are outstandingly suitable for use as absorbents for aqueous liquids, for the formulation of cosmetic preparations, as consolidators and/or binders of fibrous sheetlike structures containing reactive groups, as polymeric additives for aqueous  
15 drilling muds and cement additives in petroleum extraction, and for use in hygiene articles, packaging materials and nonwovens.

For use as superabsorbent polymers (SAPs) in hygiene articles such as diapers, tampons or sanitary towels, for example, particularly suitable  
20 hydrogels of the invention are those based on acrylic acid, which may be present in part in the form of the alkali metal salt or ammonium salt. In this case neutralization can take place either before or after the polymerization. To prepare SAPs, the hydrophilic monomers are polymerized preferably in the presence of customary crosslinkers comprising at least two  
25 ethylenically unsaturated double bonds, examples being N,N'-methylenebisacrylamide, triallylamine, 1,4-butanediol diacrylate, pentaerythritol trialkyl ethers, and/or tetraalkoxyethane.

Hydrogels of the invention based on carboxyl-containing polysaccharides  
30 are also outstandingly suitable for use as SAPs.

By means of postcrosslinking, especially at the surface, with compounds of the formula 1, it is possible to improve substantially the efficacy in terms of absorbency under load of polymers which have already been

precrosslinked and are intended for use as SAPs.

Through the addition of acidic catalysts it is possible to accelerate the crosslinking reaction and/or to lower the reaction temperature.

5

Compounds suitable as catalysts in the process of the invention are inorganic oxo acids, their acid salts and anhydrides, esters or partial esters, examples being phosphoric acid, sulfuric acid, boric acid, polyphosphates, polyborates, polyphosphonates, phosphonic anhydrides, and also hydrogen sulfates and hydrogen phosphates. Likewise suitable are acids of the formula HX in which X can be a halogen, and all known Lewis acids, such as BF<sub>3</sub> etherate or sulfonic acids, especially organic sulfonic acids such as p-toluenesulfonic acid, for example. Particularly suitable compounds are hydrogen phosphates, boric acid and its anhydrides, esters or partial esters, and also p-toluenesulfonic acid and BF<sub>3</sub> etherate. It is preferred to add from 0.05 to 3% by weight of catalyst based on the amount of the polymer.

10

15

#### Test methods

20

Superabsorbent polymers are characterized using certain test methods which include the measurement of the extractable fraction after n hours and the absorption of 0.9% by weight NaCl solution with and without a weight loading.

25

#### 1. Extractable fraction, n hours (n = 1-16)

30

1 g of SAP is dissolved in 200 ml of 0.9% by weight NaCl solution and stirred with a magnetic stirrer for n (n = 1-16) hours. The supernatant solution is filtered and the polyacrylic acid or polyacrylate is titrated. The pH electrode for the titration is calibrated at a pH of 2.7 and 10. Titration is carried out first with approximately 0.1 N NaOH to a pH of 10. The amount of NaOH consumed is recorded as V<sub>a</sub> (in ml) and the normality of the base as N<sub>a</sub> (n meq/ml). The solution thus titrated is then adjusted to a pH of 2.7

with approximately 0.1 N HCl. The amount of HCl consumed is recorded as  $V_b$  and the normality of the acid as  $N_b$  (in meq/ml).

5 This procedure is repeated with 0.9% by weight NaCl solution in order to determined the blank value of the titration. This time,  $V_{ab}$  is recorded as the amount of base required and  $V_{bb}$  is the amount of acid required to titrate the pure salt solution.

The extractable fraction is calculated as follows:

10

$$E = ([W_a + W_b] + 100) / W$$

where  $W$  is the total mass of the sample of superabsorbent and where

$$W_a = (V_a - V_{ab}) \cdot N_a \cdot E_a \cdot D$$

15  $W_b = (M_b \cdot E_b \cdot D)$

$$M_b = M_t - M_a$$

$$M_t = (V_b - V_{bb}) \cdot N_b \text{ and}$$

$E_a$  is the equivalent mass of a non-neutralized monomer in the polymer chain

20 (72 daltons)

$E_b$  is the equivalent mass of a neutralized monomer in the polymer chain (94 daltons) and

$D$  = dilution factor = 4

## 25 2. Centrifuge retention capacity (CRC)

This method measures the free water absorption of the SAP by the teabag method. About 0.2 g of SAP are sealed in a teabag and immersed in a 0.9% by weight NaCl solution for 20 minutes. The teabag is then spun in a  
30 centrifuge for 5 minutes at  $250 \times g$ . A teabag without SAP is used to determine the blank value for the measurement:

$$\text{Retention CRC (g/g)} = \frac{\text{Final weight} - \text{blank value} - \text{Initial weight}}{\text{Initial weight}}$$

### 3. Absorbency under load (20, 40, 60 g/cm<sup>2</sup>)

For the absorbency under load, 0.9 g of SAP are distributed uniformly on the base of a Plexiglas cylinder. The cylinder has a height of 50 mm and an internal diameter of 60 mm. At the base of the cylinder there is a wire mesh having a mesh size of 36  $\mu$ m (400 mesh). A cover plate is placed on top of the superabsorbent and the sample is loaded with an appropriate weight (20, 40 or 60 g/cm<sup>2</sup>). The superabsorbent is then allowed to swell for 60 minutes under the corresponding load.

10

The absorbency under load (AUL) is calculated as follows:

$$AUL(g/g) = [(W_b - W_a)/W_s]$$

15

where  $W_a$  is the mass of the apparatus,  
 $W_b$  the mass of the apparatus after absorption of water by the SAP, and  
 $W_s$  the mass of the SAP.

### 4. Gel strength

20

The shear modulus is measured with the aid of a Carri-Med controlled stress rheometer using a 6 cm plate/plate geometry. In order to determine the shear modulus, 2.5 g of SAP is left to swell in 100 g of 0.9% by weight NaCl for 24 hours and then the shear modulus is measured as a function of the frequency. The value at 10 Hz is stated as the storage modulus.

25

Examples 1 and 2 describe the use of the compound of the formula 1, in which  $R=R'=H$  and/or  $CH_3$ , as a crosslinker during the polymerization reaction.

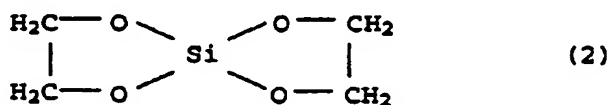
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#### Example 1

A polyethylene vessel well insulated with foamed plastic material and having a capacity of 10 l is charged with 4780 g of deionized water. 1696 g

of sodium bicarbonate are suspended in this initial charge, and 1994 g of acrylic acid are metered in slowly so as to avoid excessive foaming of the reaction solution, which cools to a temperature of about 5-3°C. At this point 6 g of the compound 2

5



10

and 10 g of a sodium diisooctylsulfosuccinate (<sup>®</sup>Rewopol V 2133 from REWO, Steinau) along with 2.5 g of N,N'-methylenebisacrylamide are added. At a temperature of 4°C the initiators - a redox system consisting of 2.2 g of 2,2'-azobisamidinopropane dihydrochloride dissolved in 20 g of deionized water, 4 g of potassium peroxodisulfate dissolved in 150 g of deionized water, and 0.4 g of ascorbic acid dissolved in 20 g of deionized water - are added in succession and the mixture is stirred. The reaction solution is subsequently left to stand without stirring and as a result of the ensuing polymerization, in the course of which the temperature rises to about 89°C, a solid gel is formed. This gel is subsequently subjected to mechanical comminution, dried at temperatures above 150°C, and ground.

The resultant product was incorporated in conventional manner into a diaper, where it gave particularly good fluid retention.

#### Example 2

The procedure of Example 1 is repeated but now with the use of 6.0 g of the compound 3 (= compound 1, where R=R' is CH<sub>3</sub>). The resultant product here is also outstandingly suitable for use in diapers and is notable for good fluid retention and distribution.

#### Example 3

Under adiabatic conditions, a 1.5 l wide-necked cylindrical reaction flask is charged with 1287 g of deionized water cooled to 15°C, and 255 g of acrylic acid and 1.28 g of tetraallyloxyethane are dissolved therein. Nitrogen is passed into the monomer solution (about 2 l/min. for about 5 20 minutes) in order to lower the oxygen content. At a content of 1.5 ppm O<sub>2</sub>, 7.7 g of a 10% aqueous solution of 2,2'-azobis(2-amidinopropane) dihydrochloride are added. After passing in further N<sub>2</sub>, at an O<sub>2</sub> content of 1.3 ppm, 2.6 g of a 1% H<sub>2</sub>O<sub>2</sub> solution are added and finally, at an O<sub>2</sub> content of 1.0 ppm, 6.4 g of a 0.1% ascorbic acid solution are added. 10 The ensuing polymerization, in the course of which the temperature rises to about 65°C, produces a solid gel which is subsequently subjected to mechanical comminution. 56.5 g of 50% aqueous sodium hydroxide solution are added to 400 g of the comminuted gel (degree of neutralization of the acrylic acid: 74 mol %), thorough kneading is carried 15 out twice, 25 g of a 1% solution of the compound 2 are added, kneading is again carried out twice, and then the product is dried in a thin layer at temperatures of more than 150°C, ground and sieved.

The resultant product is essentially characterized inter alia by the following 20 physical data, all measured with 0.9% NaCl:

Extractable fraction (1 h) 2.1%, A

Absorbency under load (20 g/cm<sup>2</sup>) = AUL 20 = 29.9 g/g.

#### 25 Example 4a

Under adiabatic conditions, a 1.5 l wide-necked cylindrical reaction flask is charged with 2574 g of deionized water cooled to 15°C, and 510 g of acrylic acid and 1.52 g of triallylamine are dissolved therein. Nitrogen is 30 passed into the monomer solution (about 2 l/min. for about 20 minutes) in order to lower the oxygen content. At a content of 1.5 ppm O<sub>2</sub>, 7.7 g of a 10% aqueous solution of 2,2'-azobis(2-amidinopropane) dihydrochloride are added. After passing in further N<sub>2</sub>, at an O<sub>2</sub> content of 1.3 ppm, 2.6 g of a 1% H<sub>2</sub>O<sub>2</sub> solution are added and finally, at an O<sub>2</sub> content of 1.0 ppm,

6.4 g of a 0.1% ascorbic acid solution are added. The ensuing polymerization, in the course of which the temperature rises to about 65°C, produces a solid gel which is subsequently subjected to mechanical comminution. Drying of this gel gives the comparative product of Table 1 (gel 4a).

#### Example 4 b

300 g of a comminuted 30% polymer gel from Example 4a neutralized to the extent of 73 mol % are admixed with 0.26 g of a compound 1, in which  $R = R' = CH_3$ , dissolved in 40 ml of methanol and this mixture is subjected to homogeneous kneading, comminution, drying at 180°C to a residual moisture content of 3%, grinding and sieving. After surface postcrosslinking, the resulting gel is referred to as Example 4b.

15

The examples below demonstrate the effect of the invention of the surface postcrosslinking for a particulate system with carboxyl or carboxylate groups.

20 The increase in the absorbency under load is documented in Table I.

#### Example 5

300 g of a comminuted 30% polymer gel from Example 4a neutralized to the extent of 73 mol % are admixed with 0.51 g of the compound 3 (= compound 1 where  $R = R' = CH_3$ ) dissolved in 40 ml of methanol and this mixture is subjected to homogeneous kneading, comminution, drying at 180°C to a residual moisture content of 3%, grinding and sieving.

#### 30 Example 6

300 g of a comminuted 30% polymer gel from Example 4a neutralized to the extent of 73 mol % are admixed with 0.39 g of the compound 2 dissolved in 40 ml of methanol and this mixture is subjected to



homogeneous kneading, comminution, drying at 180°C to a residual moisture content of 3%, grinding and sieving.

#### Example 7

5

300 g of a comminuted 30% polymer gel from Example 4a neutralized to the extent of 73 mol % are admixed with 0.76 g of the compound 2 dissolved in 40 ml of methanol and this mixture is subjected to homogeneous kneading, comminution, drying at 180°C to a residual moisture content of 3%, grinding and sieving.

10

#### Example 8

300 g of a comminuted 30% polymer gel from Example 4a neutralized to the extent of 73 mol % are admixed with 1.2 g of the compound 2 dissolved in 40 ml of methanol and this mixture is subjected to homogeneous kneading, comminution, drying at 180°C to a residual moisture content of 3%, grinding and sieving.

15

The products obtained from Examples 4 to 8 are characterized by the data collated below in Table I:

20

Table I

		Extractable fraction, 16 h (%)	Absorbency under load (20 g/cm <sup>2</sup> ) (g/g)	Gel strength <sup>*)</sup> (Pa)
5	Initial polymer untreated, prepared according to Example 4a (Comparative Example)	9.8	18.4	510
10	Examples in accordance with the invention:			
	4b	5.8	26.1	608
	5	4.6	31.9	3210
15	6	4.3	33.1	3100
	7	3.1	32.0	3500
	8	3.7	34.6	3680

<sup>\*)</sup> measured after a swelling period of 24 hours in 2.5% concentration

20

#### Example 9

0.2% by weight of the compound 2 (= formula 1 where R = R' = H) as a 10% solution are applied by spraying in a PETTERSON & KELLY mixer to customary commercial, partially neutralized, crosslinked polyacrylic acid preheated to 45°C, for use as superabsorbents in diapers, and mixing is carried out at 185°C for 20 minutes. After the product has been cooled to room temperature, the values set out in Table II below, improved in comparison to the starting material, were found:

30

Table II

	Compound 2 % by weight	Extractable fraction, 16 h (%)	Absorbency under load (60 g/cm <sup>2</sup> ) (g/g)	CRC (g/g)
5 Starting material employed	-	7.1	14.3	45
Example 9	0.2	3.5	26.2	30

## 10 Example 10

100 g of high molecular mass non-crosslinked polyacrylic acid (molecular weight  $M_w \geq 1$  million) with a degree of neutralization of 53 mol % in the form of a comminuted gel prepared as in Example 4 but without crosslinker are kneaded homogeneously together with 120 g of carboxymethylguar and 100 g of a 0.15% solution of compound 2 (formula 1 where R and R' = H) and this mixture is comminuted, dried in a stream of air at 180°C for 15 minutes, ground and sieved. This gives a water-swellaible product having a water absorption capacity which is a multiple of its own weight.

20

Examples 11 to 15 describe the preparation of water-swellaible products of good absorbency by crosslinking polymers of various origin with compounds of the invention by forming pastes of mixtures of polyacrylates and carboxymethylpolysaccharides or alginates in water, adding compounds of the formula 1, and subjecting the products to homogeneous kneading, drying in a stream of air at 180°C, grinding and sieving.

25

## Example 11

30 50 parts by weight of carboxymethylcellulose, 50 parts by weight of crosslinked polyacrylate, prepared according to Example 4a, 0.6 part by

weight of a compound of the formula 1 where R and R' = CH<sub>3</sub>.

#### Example 12

- 5     30 parts by weight of carboxymethylcellulose, 70 parts by weight of crosslinked polyacrylate, prepared according to Example 4a, 0.35 part by weight of a compound of the formula 1 where R and R' = H.

#### Example 13

10

- 45 parts by weight of carboxymethylstarch, 55 parts by weight of crosslinked polyacrylate, prepared according to Example 4a, 0.56 parts by weight of a compound of the formula 1, in which R, R' = H.

#### 15     Example 14

65 parts by weight of alginate, 45 parts by weight of crosslinked polyacrylate, prepared according to Example 4a, 1.8 parts by weight of a compound of the formula 1, in which R, R' are CH<sub>3</sub>.

20

#### Example 15

- 20 parts by weight of carboxymethylcellulose, 20 parts by weight of carboxymethylstarch,  
25     60 parts by weight of crosslinked polyacrylate, prepared according to Example 4a,  
1.4 parts by weight of a compound of the formula 1, in which R = R' = H.

#### Examples 16 - 27

30

Compounds of the formula 1 as 10% aqueous or aqueous-alcoholic solutions are added in a mixer to customary commercial, partially neutralized, crosslinked polyacrylic acid preheated at from 30 to 60°C, for use as superabsorbents in hygiene products, and treatment is carried out

at 130°C - 200°C. In Examples 22 to 26, mixtures of the compounds of the formula 1 are employed.

- After the product had been cooled to room temperature the following values set out in Table III, improved in comparison to the starting material, were found.

Table III

	Compound 1 % by weight		Extractable fraction, 16 h	Absorbency under load (60 g/cm <sup>2</sup> )	CRC
	R, R' = H	R, R' = CH <sub>3</sub>	(%)	(g/g)	(g/g)
Starting material employed	-	-	7.8	13.6	49
Example 16	0.3		3.2	27.1	29
Example 17		0.2	3.1	27.6	30
Example 18		0.25	3.0	27.6	28
Example 19		0.3	3.0	28.9	26
Example 20	0.6		2.1	29.3	24
Example 21	1.5		2.0	20.0	18
Example 22	0.1	0.1	3.6	26.7	33
Example 23	0.2	0.2	2.8	27.5	30
Example 24	0.3	0.4	2.5	30.3	29
Example 25	0.5	0.5	2.1	29.9	28
Example 26	1.0	1.0	2.2	33.1	25
Example 27	0.25		3.5	26.2	32

## Examples 28 to 32

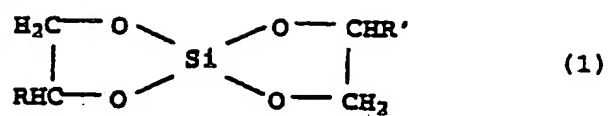
Compounds of the formula 1 as aqueous or aqueous-alcoholic mixtures with the addition of from 0.1 to 0.6% by weight, based on polymer, of acidic catalysts are added to customary commercial, partially neutralized, crosslinked polyacrylic acid for use as superabsorbents, and treatment is carried out at from 120°C to 180°C. After the product had been cooled to room temperature the following values set out in Table IV, improved in comparison to the starting material, were found.

Table IV

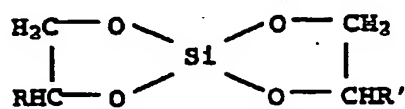
	Compound 1 % by weight		Catalyst	Reaction temp.	Absorb- ency under load (60 g/cm <sup>2</sup> )	CRC
	R, R' = H	R, R' = CH <sub>3</sub>	(% by weight)	(°C)	(g/g)	(g/g)
Starting material employed	-	-			13.6	49
Example 28	0.2		NaH <sub>2</sub> PO <sub>4</sub> 0.5	160	26.8	30
Example 29	0.6		H <sub>3</sub> PO <sub>4</sub> 0.1	140	28.4	26
Example 30		0.3	H <sub>3</sub> BO <sub>3</sub> 0.6	165	27.1	28
Example 31		0.8	p-toluene- sulfonic acid 0.2	140	28.6	25.5
Example 32	0.2	0.2	BF <sub>3</sub> etherate 0.3	130	26.0	32

The compounds specified in the description and in the claims

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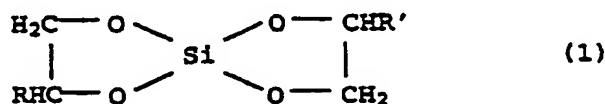


also include the stereoisomers, examples being those of the formula



## Patent claims

1. A process for the surface crosslinking of particles of superabsorbent polymers which comprises using a compound of the formula 1 as crosslinker



in which R and R' are independent of one another or are the same and are hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl.

2. The process as claimed in claim 1, where the superabsorbent polymer is a polyacrylate, a carboxymethylpolysaccharide or a mixture of polyacrylates and carboxymethylpolysaccharides.
3. The process as claimed in claim 1 and/or 2, wherein crosslinking takes place at the surface of the polymer particles.
4. The process as claimed in one or more of claims 1 to 3, wherein crosslinking is carried out in the temperature range from 120°C - 220°C.
5. The process as claimed in one or more of claims 1 to 4, wherein crosslinking is carried out with addition of acidic catalysts.
6. The process as claimed in claim 5, wherein the amount of catalyst is from 0.05 to 3.0% by weight based on the polymer.
7. The process as claimed in one or more of claims 1 to 6, wherein the compound of the formula 1 is applied in the form of aqueous mixtures.



8. The process as claimed in one or more of claims 1 to 7, wherein the compound of the formula 1 is applied in the form of aqueous-alcoholic mixtures.
- 5 9. The process as claimed in one or more of claims 1 to 7, wherein polyacrylates in solid form as powders or granules are crosslinked.
10. A surface-crosslinked superabsorbent polymer prepared by the process as claimed in one or more of claims 1 to 9.
- 10 11. The use of a surface-crosslinked superabsorbent polymer as claimed in claim 10 in a hygiene article, packaging material or nonwoven.

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